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Patentanmeldung Nr. Patent application No. Demande de brevet n°

04101416.8 ✓

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Printing fluid for fluid-jet printing

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## Printing fluid for fluid-jet printing

The invention relates to a printing fluid suited for fluid-jet printing. The invention further relates to a method of manufacturing such a printing fluid, and a method of liquid-jet printing using the printing fluid.

Fluid-jet printing, also better known by its conventional name ink-jet printing, is presently used in many applications for printing with a relatively high precision liquids on substrates. One of these applications is the manufacturing of Poly-LED displays.

PolyLED displays comprise a large number of light emitting diodes, wherein each light emitting diode (commonly referred to as LED) comprises a stack of individual layers dissolved in a solvent in a pixel, wherein a pixel is a limited area having predetermined dimensions. The ink droplets which are released by the print head for the purpose of providing the substrate with the layers comprise a solvent and the material of the layers.

Drying of ink-jet printed structures, such as pixels of PolyLED displays, by which the solvent is vaporized usually leads to variations of the layer thickness of the structure. These variations can be present on a small scale (e.g. within a pixel) and also on a larger scale (e.g. on the substrate).

However, such an ink-jet printing process done with a conventional ink has a very small process window since any small variation in e.g. evaporation rate will lead to variation in the local layer thickness profile over the substrate. Such variations in evaporation rate are hard to avoid and will in practice always be present.

In almost all electronic devices layer uniformity is required on a large scale. On a small scale, layers with constant thickness are also often required. This means that the layer thickness must be constant within a printed structure. However, with a conventional printing fluid it appears that a constant layer thickness is difficult to obtain.

It is an object of the invention to provide a printing fluid suitable for fluid-jet printing in which the uniformity of the thickness of the printed layers is improved. To this end a printing fluid suited for fluid-jet printing is provided according to claim 1.

Experimentally as well as by numerical simulations, it has been demonstrated by the inventors that by using a printing fluid that comprises particles having two particle size distributions a layer can be printed with a more uniform layer thickness.

During drying evaporation-induced mass transport takes place, which may lead to a highly non-uniform layer thickness distribution of a printed structure or line. The mass-transport consists of two main processes. The first process is convection of ink towards the contact line, caused by evaporation (also known as the "coffee-ring" effect), whereby the contact line is defined as the boundary line between the area comprising the ink and the outside area that does not comprise ink. The second process is the diffusion of particles away from the contact line where the particle concentration is highest. As a result of this, two drying modes exist.

In the first mode, convection is dominant and the resulting layer thickness profiles has two ridges near the contact line. In the second mode, diffusion is dominant and the layer thickness profile has the shape of a spherical cap.

When the drying process is in between these two modes, a layer thickness profile can be obtained that is flat and has a uniform thickness. The disadvantage however is that such a process has a very small process window, because any small variation in e.g. evaporation rate will lead to variation in the local layer thickness profile over the substrate.

This problem is solved by the invention, in which an ink is provided with two particle size distributions. Large particles dry in the convection-dominant mode, whereas small particles dry in the diffusion-dominant mode. By a proper mix of large and small particles a uniform thickness profile is obtained.

This aspect as well as other aspects of the invention are defined by the independent claims.

Advantageous embodiments of the invention are defined in the dependent claims.

These and other aspects of the invention will be elucidated with reference to the embodiments described hereinafter.

In the drawings,

Fig. 1 show the particle sizes as a function of volume fraction  $V$  of the printing fluid according to the invention,

Fig. 2 shows results of numerical simulations of the thickness of a layer applying the printing fluid according to the invention, and

Fig. 3 shows the results of measurements of layer thickness distributions of two ink-jet printed surfaces.

The Figures are not drawn to scale. In general, identical components are denoted by the same reference numerals in the Figures.

5                    Figure 1 shows the particle sizes of the printing fluid (ink) according to the invention as a function of volume fraction  $V$ . The printing fluid comprises first particles having a first size  $s_1$  that falls within a first size distribution I, and second particles having a second size  $s_2$  that falls within a second size distribution II different from said first size distribution I. The first and second particles are substantially of the same material. The  
10                    particle size distribution is in most cases a normal (Gaussian) distribution being centered around a certain mean value. In figure 1 the mean values of size distribution I and II are indicated by  $s_{m1}$  and  $s_{m2}$ , respectively. It can also be seen that the volume fraction  $V$  of distribution I is larger than that of distribution II.

                    Figure 2 shows results of numerical simulations of the thickness profiles  
15                    resulting from a printing fluid comprising 80 weight % particles of 3 nm diameter (hence  $s_{m1}$  is equal to 3 nm), indicated by the squares and the thickness from a printing fluid comprising 20 weight % of 30 nm diameter particles ( $s_{m2}$  equal to 30 nm), indicated by the triangles. For reasons of simplicity no Gaussian distribution was assumed in the simulations (hence the width of the distributions was taken to be zero). The dimensions of the two axes are indicated  
20                    microns. The layer thickness of this mixture (referred to as sum in the Figure, indicated by the diamonds) is the sum of the layer thicknesses of the two components.

                    From further numerical simulations it is concluded that a substantially flat layer thickness is obtained if the large particles are at least 10 times larger than the small particles, hence if the relation  $s_{m2} \geq 10 \times s_{m1}$  holds.

25                    Simulations show also that good flat thickness profiles are obtained if, the first size distribution I has a first size average  $s_{m1}$  being smaller than 3 nm and the second size distribution II has a second size average  $s_{m2}$  within a range between 30 nm and 100 nm.

                    Further, it is concluded that the mass fraction of the large particles should be between 10 and 40 weight %. The size of the small particles should be 2 nm diameter or  
30                    smaller, and the large particles have to be about 30 nm in diameter or larger. If these conditions are fulfilled then the printed layer thickness has a substantially flat profile.

                    Figure 3 shows the results of measurements of the layer thickness of two ink-jet printed lines, the dimensions are expressed in microns. Two lines have been printed with

printing fluids having different particle mixtures. Curves 1 and 2 show cross-sections of the printed lines, of which the bases have been scaled to each other to allow a comparison.

Curve 1 represents the measured cross-section of a line which was printed using a printing fluid comprising a mixture of 80 weight % of 2 nm particles and 20 weight  
5 % of 30 nm particles. Curve 2 represents the measured cross-section of a line that was printed using a printing fluid comprising 100 weight % particles of 2nm size.

It is concluded from these experiments that adding a small fraction of significantly larger particles to a printing fluid comprising certain particles the resulting thickness profile of a printed layer is more uniform. These measurement results confirm the  
10 results of the numerical simulation shown in figure 2.

The invention is applicable to inter alia printing fluids that comprise conductive metal particles (e.g. silver), and also to printing fluids that comprise (light-emitting) polymers. Water is a suitable solvent in which the particles are solved.

It should be noted that the above-mentioned embodiments illustrate rather than  
15 limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. The word "comprising" does not exclude the presence of other elements or steps than those listed in a claim. The word "a" or "an" preceding an element does not exclude the presence of a  
20 plurality of such elements.



## CLAIMS:

1. Printing fluid suited for fluid-jet printing, the printing fluid comprising first particles having a first size ( $s_1$ ) that falls within a first size distribution (I), and second particles having a second size ( $s_2$ ) that falls within a second size distribution (II) different from said first size distribution (I), said first and second particles being of substantially a same material.  
5
2. A method of manufacturing a printing fluid suited for fluid-jet printing, the method comprising:  
a first step of manufacturing first particles having a first size ( $s_1$ ) that falls  
10 within a first size distribution (I), and  
a second step of manufacturing second particles having a second size ( $s_2$ ) that falls within a second size distribution (II) different from said first size distribution (I), said first and second particles being of substantially a same material.
- 15 3. A method of liquid-jet printing, the method using a liquid as claimed in claim 1 or a liquid as manufactured by the method of claim 2.
4. A product manufactured by the method of claim 3.
- 20 5. A liquid according to claim 1, wherein the first size distribution has a first size average  $m_1$  and the second size distribution has a second size average  $m_2$ , and where the relation  $m_2 \geq 10 \times m_1$  holds.
- 25 6. A liquid according to claim 5, wherein the first size distribution has a first size average  $m_1$  and the second size distribution has a second size average  $m_2$ ,  $m_1$  being smaller than 3 nm and  $m_2$  being in a range between 30 nm and 100 nm.
7. A liquid according to claim 1, wherein a mass fraction of second particles is in a range between 10% and 40% by weight.



## ABSTRACT:

The invention relates to a printing fluid suited for fluid-jet printing. The printing fluid comprises first particles having a first size ( $s_1$ ) that falls within a first size distribution (I), and second particles having a second size ( $s_2$ ) that falls within a second size distribution (II) different from said first size distribution, said first and second particles being  
5 of substantially a same material. It has been demonstrated that by using such a printing fluid a layer can be printed with an improved uniform layer thickness.

Fig.1



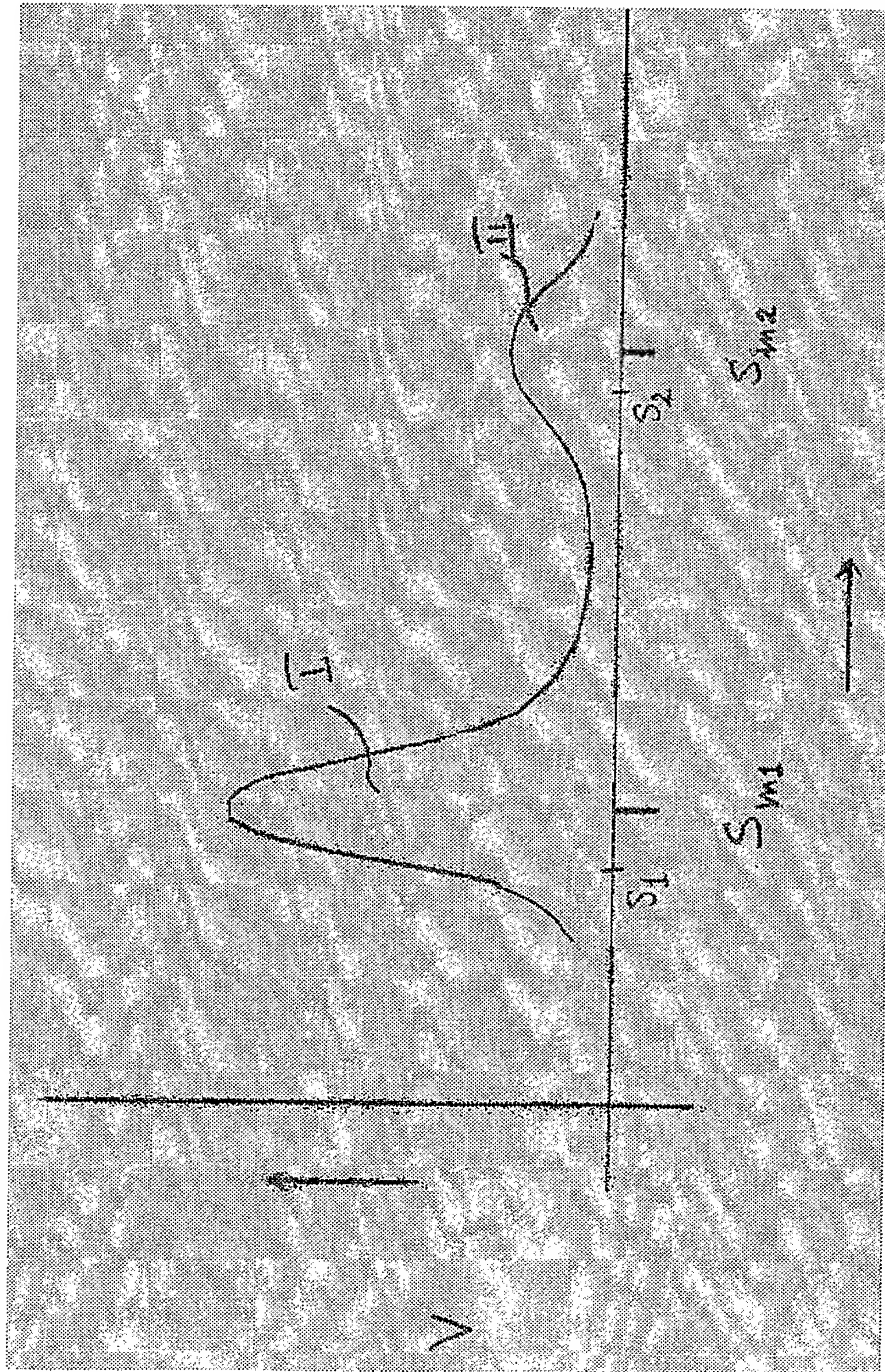


FIG.1



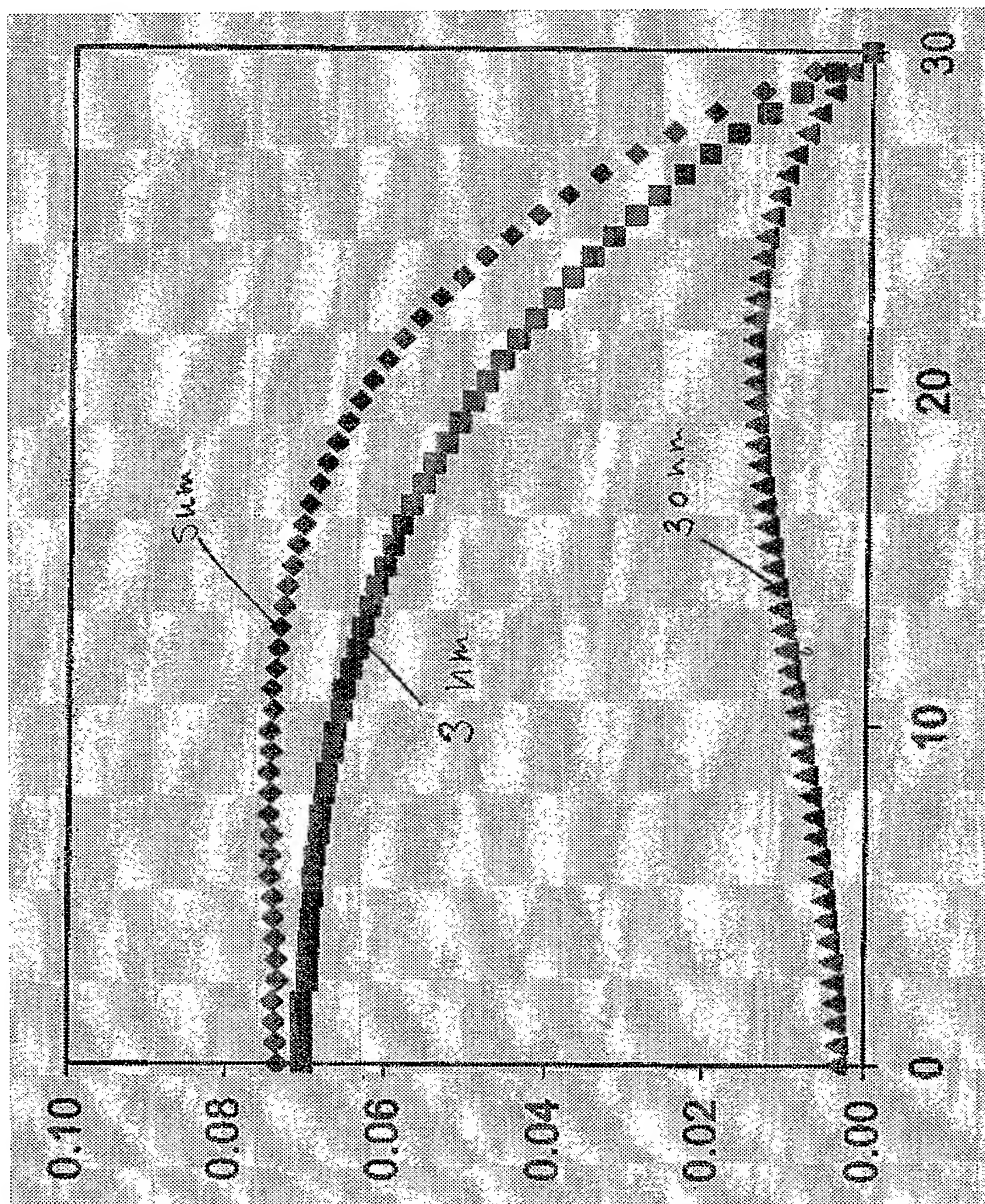


FIG.2



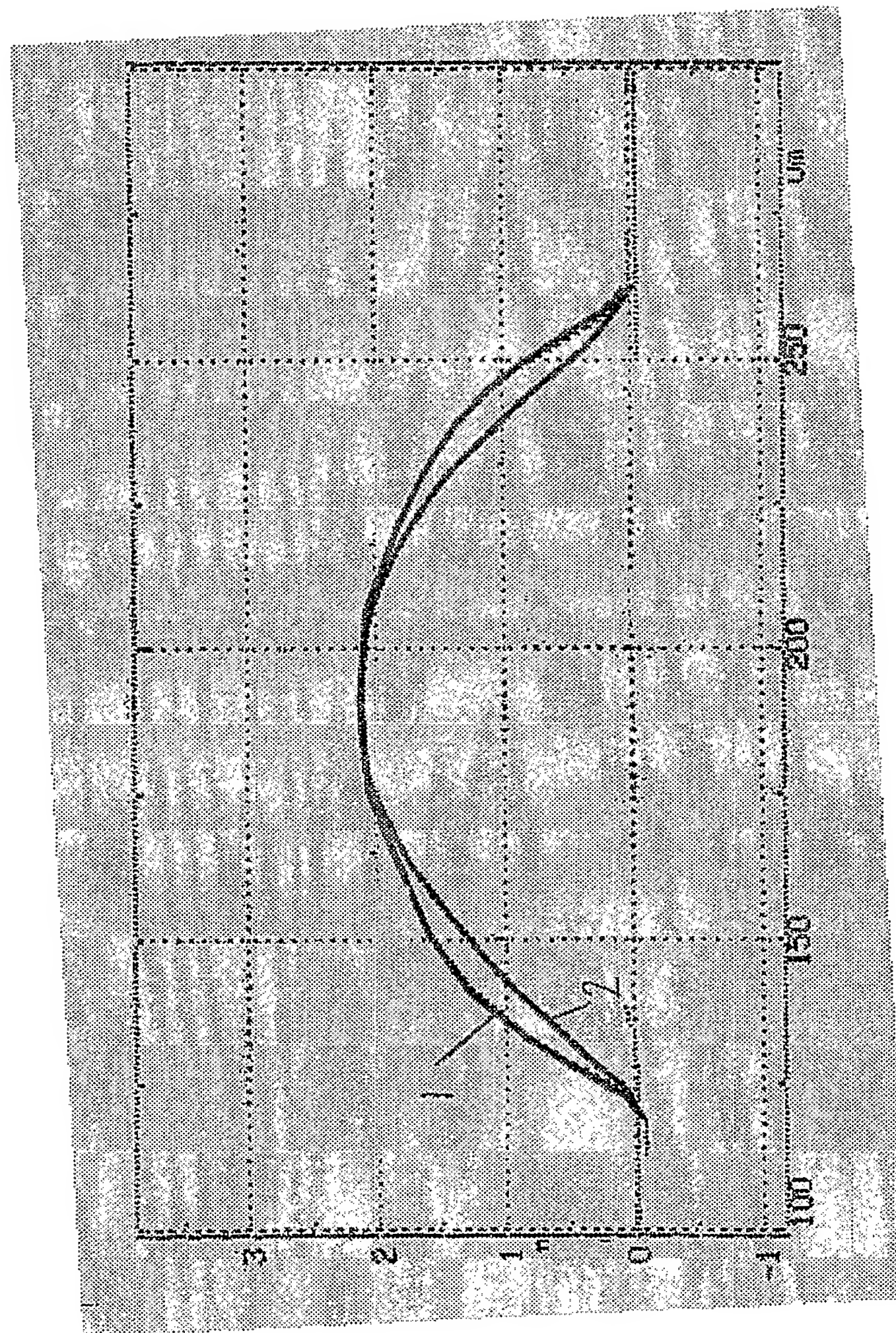


FIG.3

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